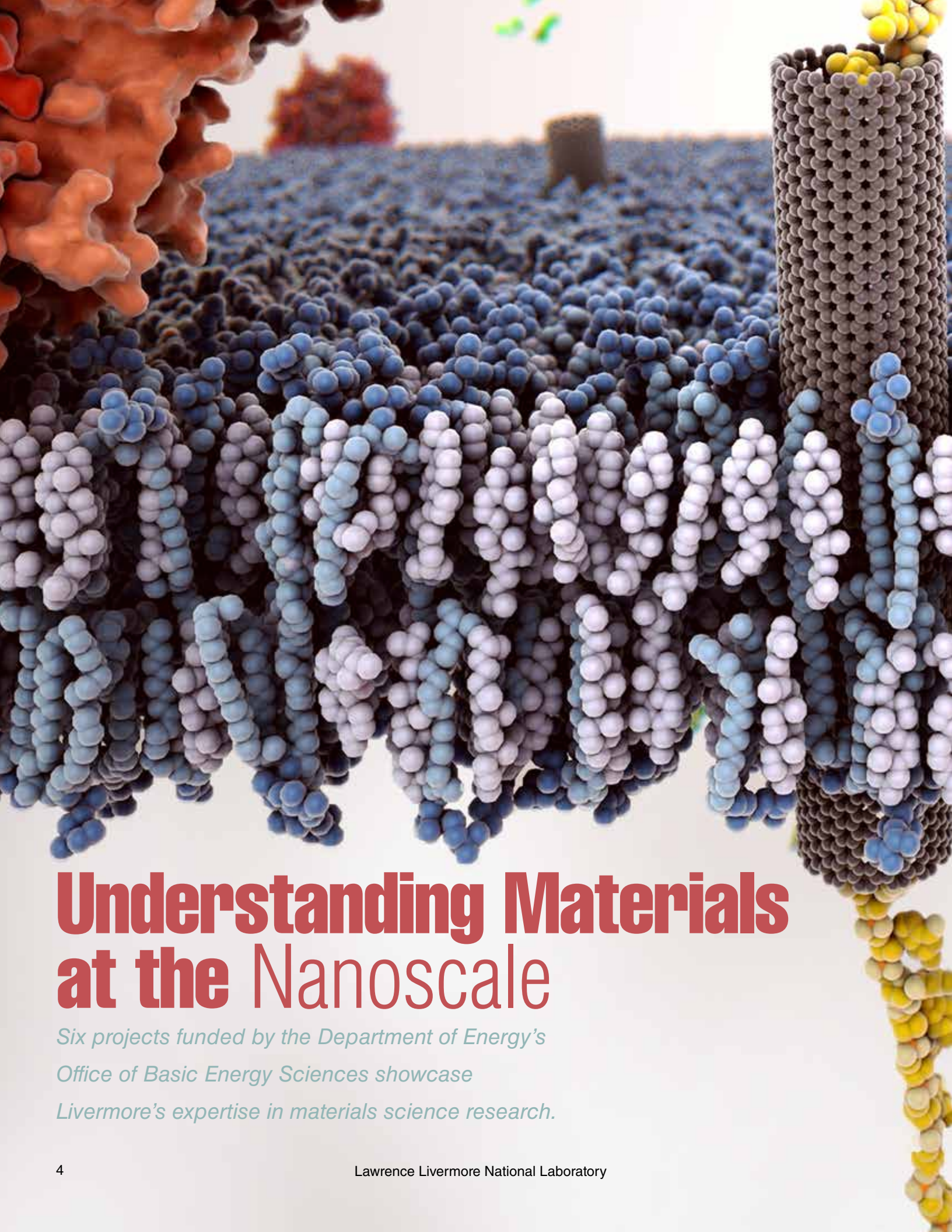
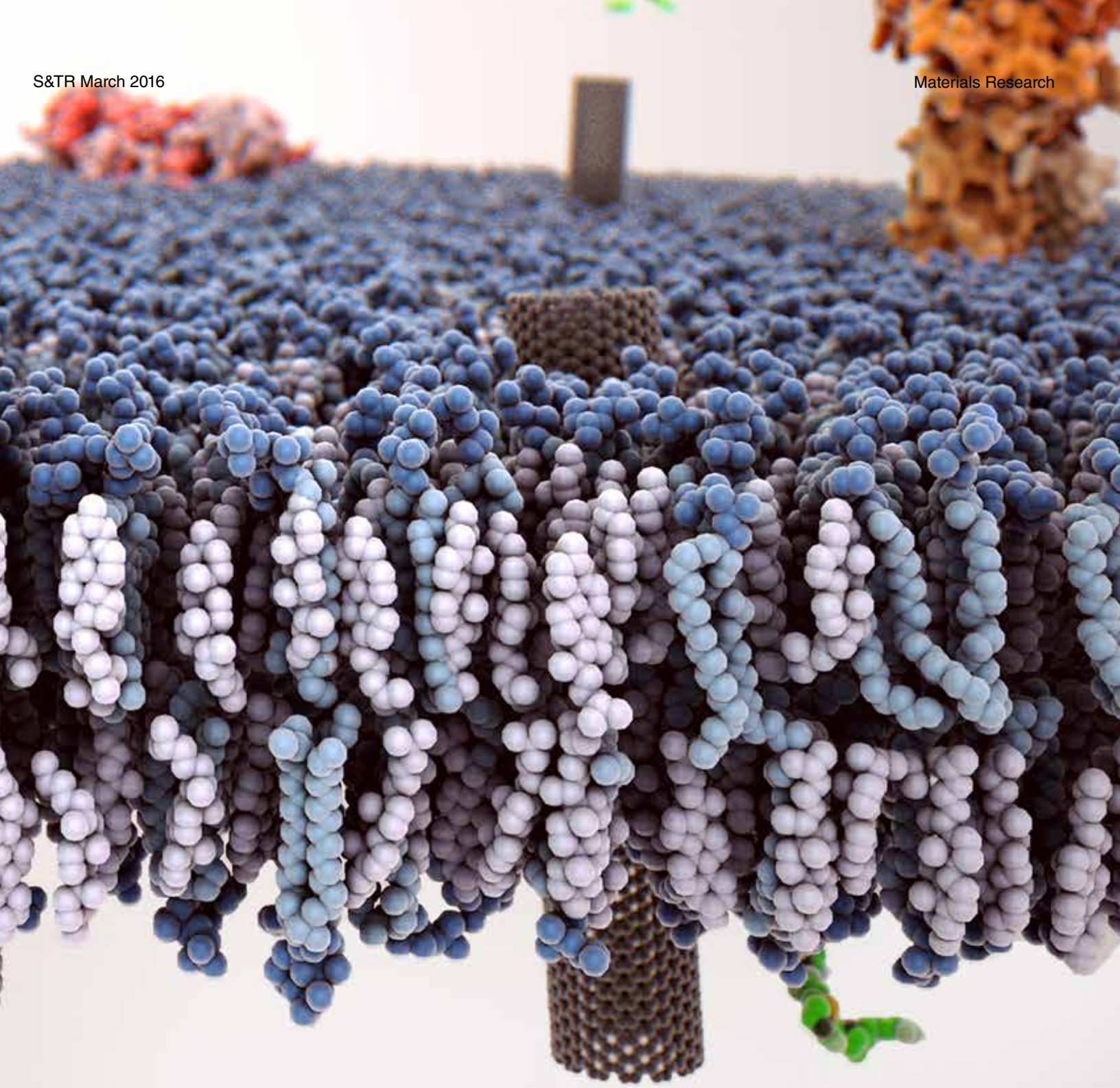


Understanding Materials at the Nanoscale

Six projects funded by the Department of Energy's Office of Basic Energy Sciences showcase Livermore's expertise in materials science research.



In this rendering, a target molecule (yellow) passes through a nanotube porin (light brown) deliberately embedded in a cell membrane to introduce such molecules into a cell body. (Image courtesy of Scripps Research Institute.)

OVER the past 60 years, Lawrence Livermore scientists and engineers have successfully found materials solutions to a wide range of challenges in national security, including energy and environmental security. The development of new materials and manufacturing processes has long been recognized as the engine driving new scientific and technological innovations in these fields.

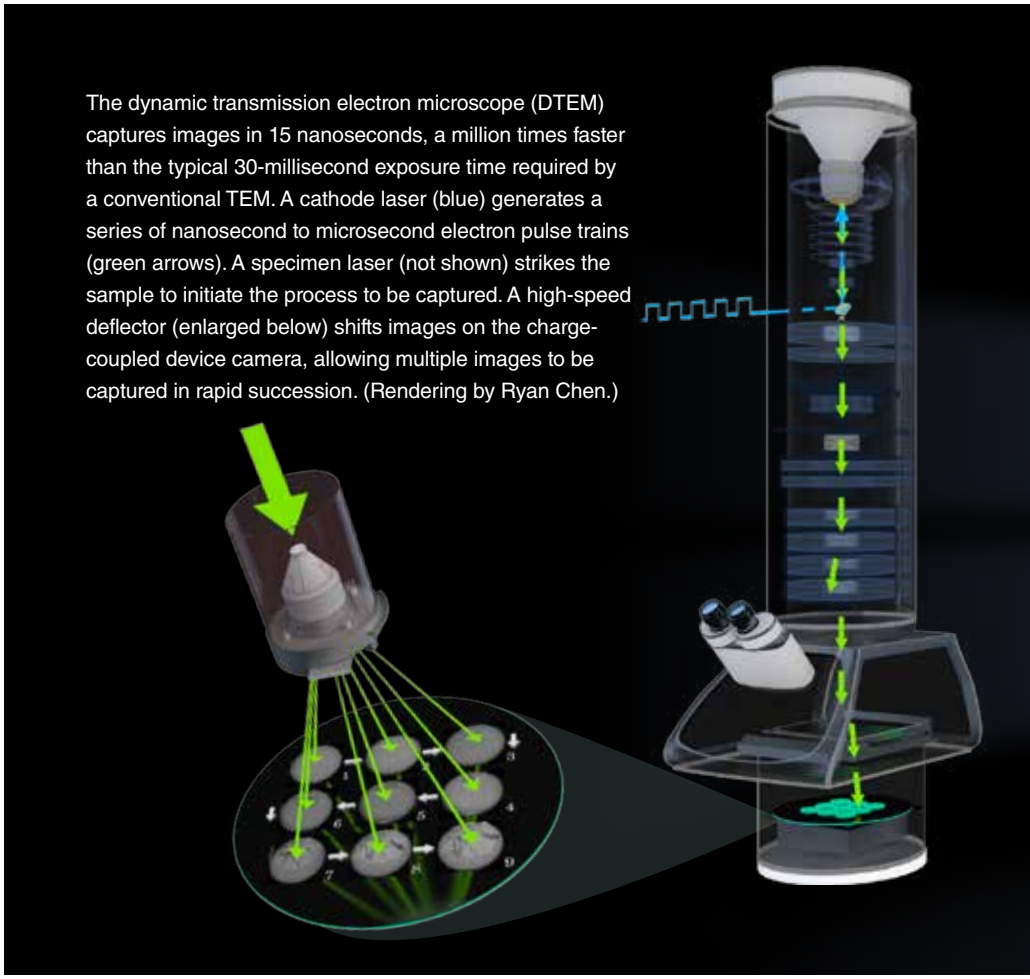
Livermore researchers routinely design and develop new materials with novel structures, functions, and properties, along with innovative methods for materials synthesis and manufacturing. Laboratory researchers are currently developing components with previously unobtainable properties, such as high stiffness combined with low density. (For example, one Livermore-developed

lightweight material can withstand a load of at least 160,000 times its own weight.) Current research thrusts include validated predictive models, atomic-scale characterization, materials synthesis and assembly, and advanced manufacturing, including three-dimensional (3D) additive manufacturing.

A portfolio of six materials research projects at Livermore is funded by the Department of Energy's (DOE's) Office of Basic Energy Sciences (BES). BES funds work at more than 160 research institutions nationwide and operates major scientific user facilities. BES supports fundamental research to understand, predict, and control matter at the atomic and molecular levels in the fields of condensed matter and materials physics, chemistry, geosciences, and aspects of physical biosciences. All efforts are focused on discovering new materials and chemical processes.

The six Livermore BES projects fall under three thematic areas: time-, space-, and energy-resolved materials investigations; nanoscale control of functional materials; and predictive modeling and simulations. These projects are strongly aligned with Livermore's motto of "Science and Technology on a Mission." Says Livermore physicist Eric Schwegler, "The Laboratory conducts much basic-science research in materials as a strategic investment because in the long term it aids our diverse national security missions. Scientific and technological breakthroughs have historically originated with basic-science activities."

The six projects also dovetail with several efforts in materials science funded by Livermore's Laboratory Directed Research and Development (LDRD) Program, which is designed to anticipate future national security needs and avoid technological surprise from adversaries. Together, the BES and LDRD efforts comprise part of the Laboratory's materials strategy, particularly its Accelerated Materials and Manufacturing Initiative. This initiative is aimed at accelerating the design, fundamental understanding, and deployment of new manufacturing processes and new materials with novel structures, functions, and properties. These endeavors draw together not only postdocs and graduate students working at Livermore but also collaborators at other national laboratories and universities.

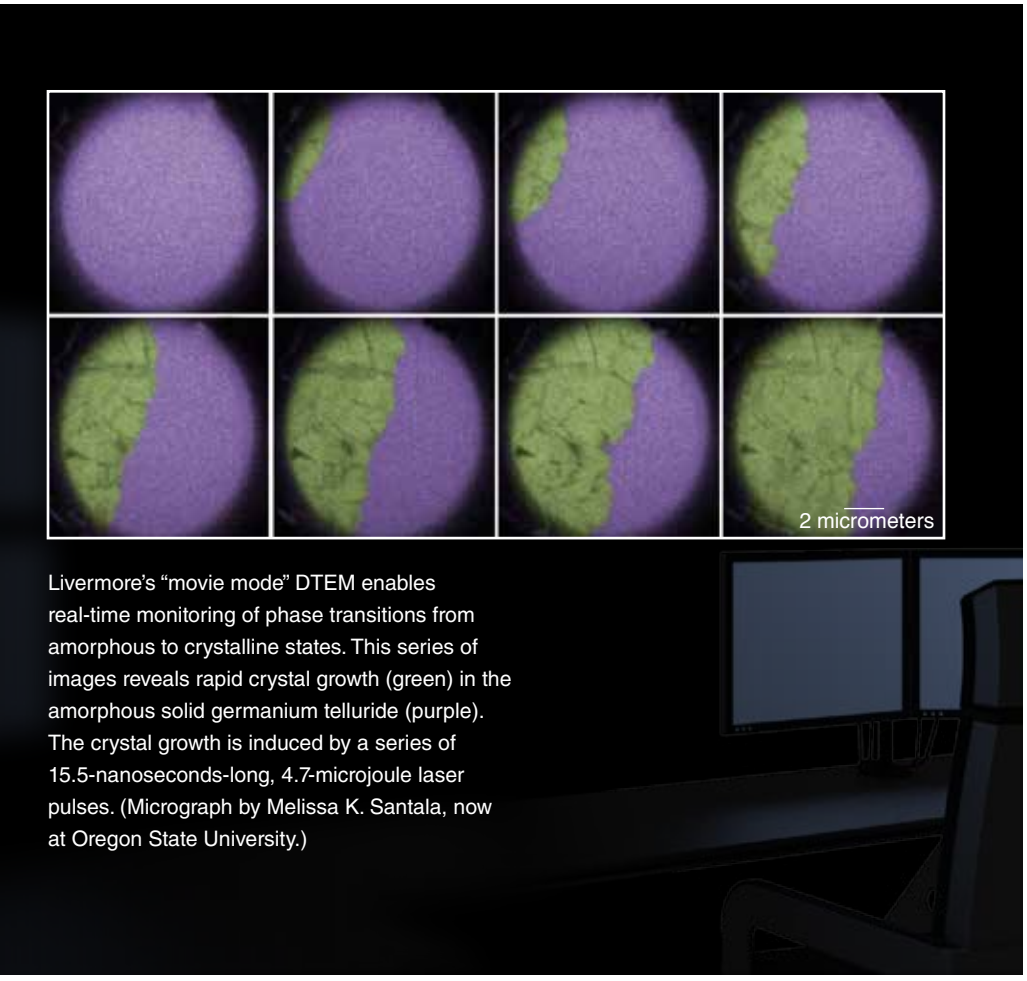


The dynamic transmission electron microscope (DTEM) captures images in 15 nanoseconds, a million times faster than the typical 30-millisecond exposure time required by a conventional TEM. A cathode laser (blue) generates a series of nanosecond to microsecond electron pulse trains (green arrows). A specimen laser (not shown) strikes the sample to initiate the process to be captured. A high-speed deflector (enlarged below) shifts images on the charge-coupled device camera, allowing multiple images to be captured in rapid succession. (Rendering by Ryan Chen.)

Much of the research is conducted at the subnanometer (less than one billionth of a meter) scale—the level of atoms and electrons. New scientific understanding and technologies are emerging through the probing, manipulation, and simulation of single atoms and molecules, discrete clusters of atoms and molecules, and large systems with nanoscale components.

Solid–Solid Transformations

Materials can undergo phase transformations—rearrangements in their crystal structure—in their solid state as a result of changes in temperature or pressure. A few metals, such as iron, can undergo several solid-to-solid phase changes before they melt. Studies of solid–solid phase transformations have been conducted since the Industrial Revolution, sparked by the discovery that different processes confer different properties, such as strength and resistance to corrosion. Today, modern tools such as the Livermore-designed dynamic transmission electron microscope (DTEM) permit, for the first time, detailed understanding and characterization of dynamic processes in materials as they take place, in particular rapid phase transformations and crystal growth (see *S&TR*, September 2013, pp. 4–11).



Livermore's "movie mode" DTEM enables real-time monitoring of phase transitions from amorphous to crystalline states. This series of images reveals rapid crystal growth (green) in the amorphous solid germanium telluride (purple). The crystal growth is induced by a series of 15.5-nanoseconds-long, 4.7-microjoule laser pulses. (Micrograph by Melissa K. Santala, now at Oregon State University.)

"We're interested in how quickly solid–solid transformations occur," explains Livermore metallurgist Geoff Campbell. Understanding these phase transformations and learning how to manipulate them could lead to breakthroughs in how materials can be processed to yield new attributes. Campbell is working with Livermore researchers Joseph McKeown and postdoc Tian Li on a BES-funded project to study the dynamics of phase transformation (nucleation and growth), microstructure, and thermodynamics in nanoscale systems evolving on timescales of nanoseconds to microseconds.

The Livermore team is investigating, at the nanoscale, the physical mechanisms and kinetics controlling solid–solid phase transformations, concentrating on the crystallization of amorphous solids, such as germanium. This type of solid lacks the long-range order found in crystals but may exhibit order on the short (nearest neighboring atom) or medium (several nearest neighboring atoms) range. Dynamic imaging or "movie mode" DTEM enables phase transitions from amorphous to crystalline states to be monitored in real time. Investigators acquire consecutive images—only 120 nanoseconds apart—of the microstructure of amorphous solid germanium evolving under heat or pressure. "We can see the nucleus of a new phase appear and grow with each frame," says Campbell. Successive images track and quantify the nucleation and growth of the crystalline microstructure.

The kinetics of phase transformations are influenced by the initial amorphous structure. The researchers are using sputtering and bombardment with argon ions to create thin films of germanium, with each method resulting in a different amorphous structure. The team then uses fluctuation electron microscopy (FEM) to characterize the structure of amorphous solids formed under different conditions. FEM measures the medium-range order needed to distinguish amorphous states from one another.

In collaboration with Schwegler's group, Campbell's team is conducting quantum simulations that are informed by the FEM data with the goal of finding the atomic arrangements (seeds) responsible for the changes in crystal growth rate. "The simulations help us understand the relative internal energies of different microstructures," explains Campbell. "We compare the observed differences in the kinetics with the predictions of simulations to reveal fundamental controlling mechanisms for the solid transformation process."

Radiation-Resistant Materials

Advanced nuclear energy reactors will require materials to perform for long periods in elevated temperatures and high-radiation conditions. Conventional engineered metals and alloys lack the required microstructural stability in the extreme environments envisioned for future reactor designs.

Crystalline metals are collections of grains arranged irregularly, with each grain oriented differently in space. Each grain represents a small single crystal ranging in size from nanometers to centimeters. Where two or more grains meet is called a grain boundary. Together, grain boundaries form an interconnected network, akin to a crude skeleton (see *S&TR*, December 2014, pp. 16–19). The 3D arrangement of the grain boundaries, and how they interact, affects a material's mechanical,

thermal, chemical, and electrical properties, including its tendency to crack or corrode. As a result, controlling the types and arrangement of grain boundaries offers the possibility of tailoring a material's properties to withstand harsh radiation and thermal environments, for instance.

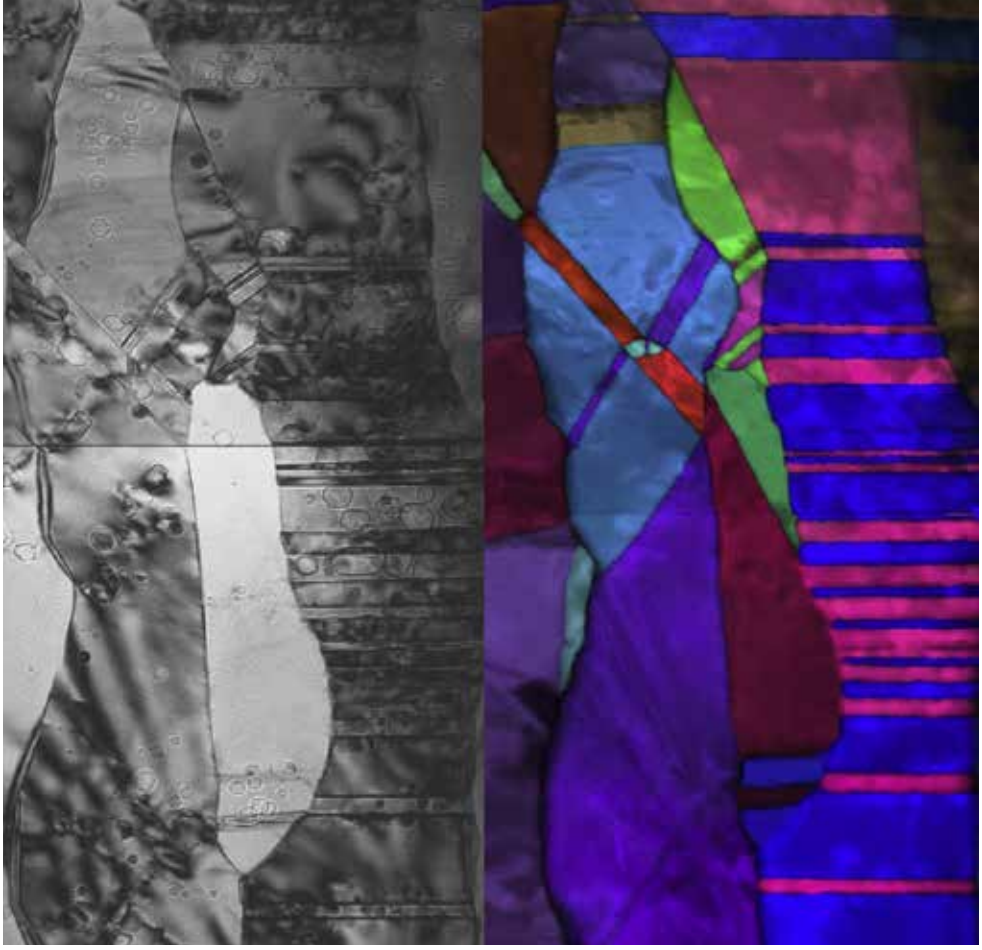
In another BES-funded effort, Livermore researchers Mukul Kumar and Vasily Bulatov are hoping to help scientists and engineers design new materials for next-generation nuclear reactors. Using transmission electron microscopy, scanning electron microscopy, and 3D high-energy x-ray diffraction microscopy, the team generates microscopy data and compares the results with advanced simulations. The researchers are working mainly with copper, which has a face-centered-cubic structure, meaning atoms are located at each of the corners and centers of all the cubic faces. Many common metals and alloys, such as austentic stainless steels and nickel-based superalloys, share this grain structure.

Kumar explains that microstructures evolve as boundaries move in response to external factors such as heat—some grains grow, others shrink. The net effect is fewer but larger grains. When subjected to radiation, point defects appear and move around in the crystalline lattice. These defects can reach grain boundaries and annihilate one another, or they can combine and eventually form a large void, distorting the metal.

The team previously showed that grain-boundary networks in polycrystalline microstructures can be stabilized against thermal damage. Researchers are currently studying whether optimized networks can also enhance microstructural stability in a high-radiation environment. Kumar's vision is a boundary network in which high-free-energy (random) grain boundaries act as efficient "sinks" for radiation-induced defects, while more stable boundaries anchor the network.

Experiments by Kumar's team showed that nanocrystalline materials exhibit poor stability under high temperatures and do not survive radiation damage, either. "People had thought that nanomaterials' extremely small grain boundaries would be sufficient to resist radiation damage," says Kumar. However, many ways exist to combine grains, and some combinations are more susceptible to radiation damage than others. "We need to combine some boundaries that absorb defects with those that resist movement and can limit any cracks that appear," he explains.

Determining microstructure properties requires proper modeling. The team modified existing quantum Monte Carlo (QMC) simulation codes to better represent the physics of grain boundary evolution. They developed a highly sensitive model that permits the study of a vast configuration of grain boundary networks to fully understand the composition of boundaries that confer thermal and radiation resistance.



(left) A TEM image shows the topology of grain boundaries in nanocrystalline copper subjected to radiation-resistance testing. (right) Arbitrary colors used to highlight grains reveal radiation-induced voids clustering near the highly ordered, parallel-sided boundaries of grains colored magenta.

Mimicking Nature's Molecules

An important part of Livermore's BES portfolio is biomimetic materials research, which focuses on designing and synthesizing materials with properties that are found only in nature—such as self-repair and adaptability to changing environments—or that mimic biological functionality using different molecular scaffolds. This project's emphasis is on creating robust and scalable materials and systems that work with the effectiveness of the molecules and processes of the biological world. Possible applications of biologically inspired synthetic materials include sensors, membranes for pharmaceutical filtration, drug delivery, platforms for nanofluidic studies, bioelectronic interfaces, and artificial cells.

One focus of the project is developing synthetic biomimetic pores called carbon nanotube porins, which mimic the characteristics of biological channels, in particular their transport functions

and their ability to self-assemble into a range of membrane systems. The project uses an array of transport studies to understand pore permeability, along with small-angle x-ray scattering and scanning transmission x-ray microscopy to probe the porins' atomic-level structures. This work seeks to understand the fundamental characteristics of the transport of biomolecules in a fully synthetic scaffold. The Livermore-led team includes Alex Noy, Tony Van Buuren, Jonathan Lee, postdocs Huanan Zhang and Ramya Tunuguntla, and Lawrence Fellow Tuan Anh Pham, as well as collaborators from Lawrence Berkeley and Pacific Northwest national laboratories, the University of California (UC) at Davis, and Spain's University of the Basque Country.

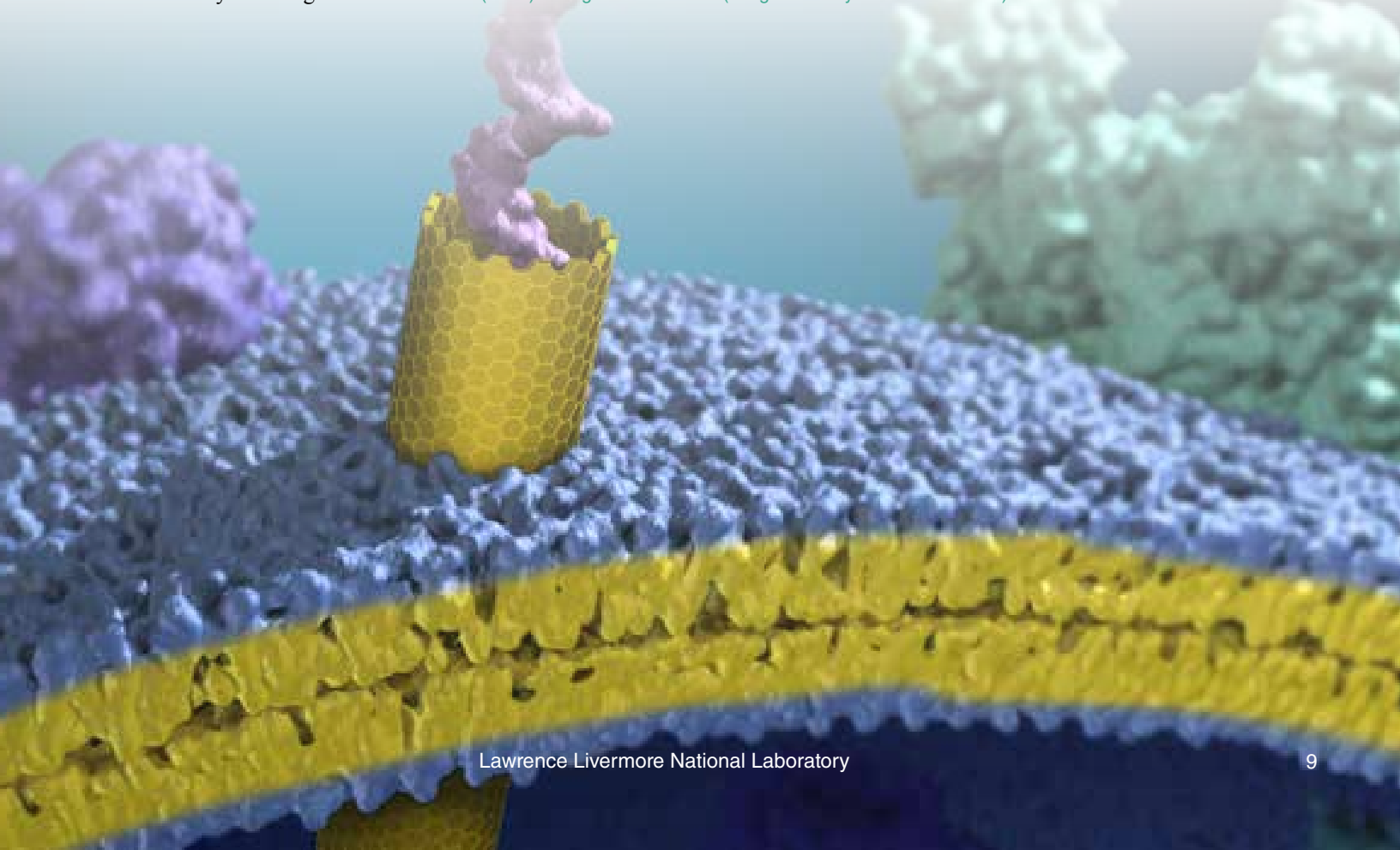
Physical chemist Noy's team has demonstrated that carbon nanotubes can be coaxed to form functional pores in biological membranes. Carbon nanotubes already have smooth and narrow pores that enable efficient transport. To convert them into nanotube porins, Noy's team dices them into very short segments and combines them with lipid molecules. The result is a dimensionally and functionally similar synthetic analogue of a biological channel (see *S&TR*, June 2015, pp. 16–19). "We can learn from nature," observes Noy, "but we don't necessarily have to imitate it."

Natural and synthetic ion channels can also act as components of much more complicated systems that convert ionic signaling into an electrical response. To make such systems possible, the team developed a bioelectronics device platform in which a silicon nanowire transistor is shielded by a lipid bilayer membrane. Researchers then inserted light-driven proton pumps—bacteriorhodopsin proteins—into the bilayer. Light caused the protein to pump protons toward the nanowire, which in turn produced changes in the output current of the nanowire transistor. Similar biologically controlled devices that seamlessly integrate biological functionality into electronic circuits could find uses in future generations of interfaces between people and machines.

Starting from First Principles

Schwegler, leader of Livermore's Quantum Simulations Group, notes that predictive simulation tools are playing an increasingly important role in Livermore's materials research. The term "quantum simulations" refers to the use of computational methods that provide numerical solutions to the fundamental laws of quantum mechanics in an approximate yet nonempirical manner. Progress in quantum simulations of condensed and molecular systems, combined with the development of algorithms and optimized codes running on

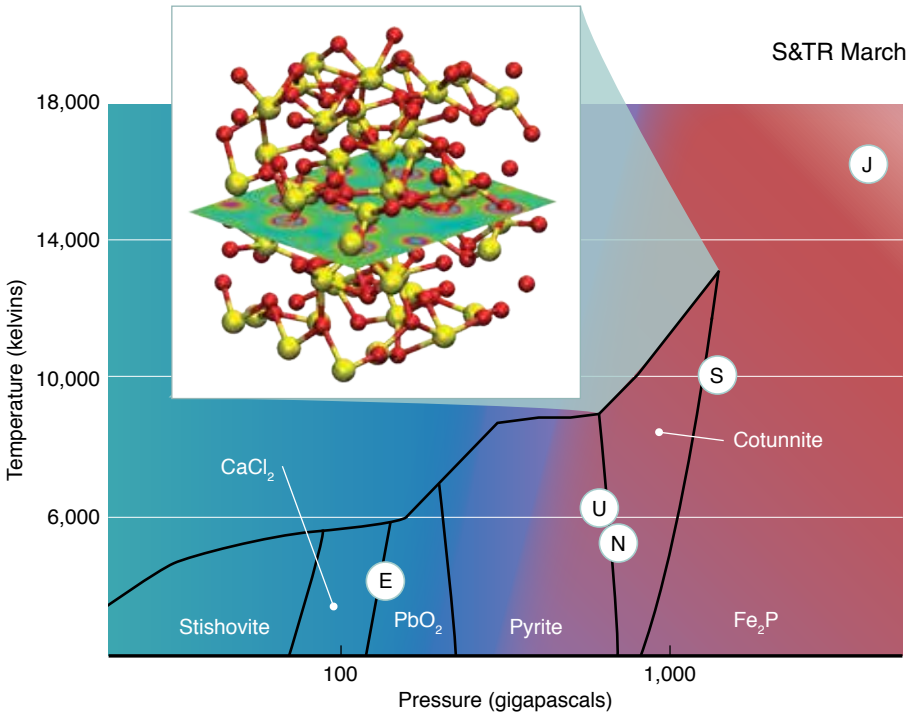
Livermore-developed carbon nanotubes spontaneously insert into both artificial and natural cell membranes, reproducing the functions of biological channels. In this rendering, a carbon nanotube (yellow) has inserted into a cell membrane (blue and yellow), with a single strand of DNA passing (violet) through the nanotube. (Image courtesy of Xavier Studios.)



high-performance computers, has opened the possibility of using truly predictive simulation tools to address the complexity of materials at the microscopic level. Numerous properties can now be inferred directly without input from experiment.

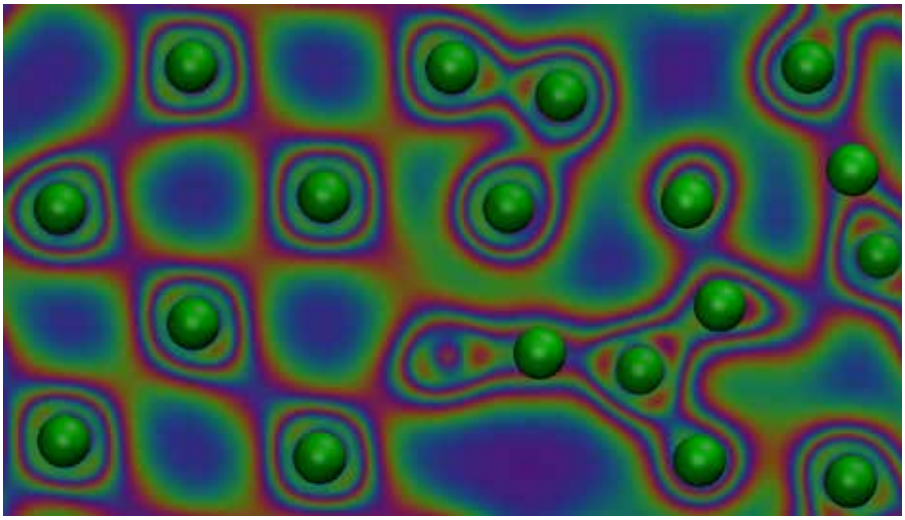
The main supercomputer codes that Livermore scientists use to model materials at the quantum level are based on density functional theory and QMC techniques. Both approaches start from first principles—that is, with no input other than the laws of quantum mechanics. Density functional theory is based on a Hohenberg–Kohn theorem positing a one-to-one correspondence between the electron density and energy of a system. Determining electron density therefore makes it possible to determine a wide range of properties—such as the forces acting between atoms—which in turn can be input into a molecular dynamics simulation to describe the system's motion in time. Together, these simulations provide an accurate, atomic-scale model of matter for applications in chemistry, materials science, and nanotechnology.

A BES-funded project at Livermore, UC Davis, and the University of Chicago is focused on advancing a high-performance, open-source software infrastructure called Qbox. Downloadable free of charge and in use at major supercomputer centers everywhere, Qbox is increasingly used as a predictive tool in the exploration of properties of new materials for batteries, solar energy conversion, light-emission devices, dielectric materials, and phase-change materials for optical storage.



A phase diagram of silicon dioxide (SiO_2) as revealed by quantum-mechanics simulations shows that as SiO_2 compresses, it goes through different solid phases having crystal structures that correspond to the compounds listed, including calcium chloride ($CaCl_2$), lead dioxide (PbO_2), and iron phosphide (Fe_2P). Circled letters stand for Earth, Uranus, Neptune, Saturn, and Jupiter and indicate the pressure and temperature believed to exist at each planet's center. (inset) Yellow and red represent silicon and oxygen, respectively, in the cotunnite-type crystal structure of SiO_2.

Schwegler is working with postdoc Amit Samanta to implement advanced sampling algorithms that direct Qbox to find and characterize rare reactions. For example, theoretical analyses of phase transition mechanisms (such as solid to liquid) are often not feasible with standard simulation methods because such transitions involve rare events that take place over time periods many orders of magnitude greater than a supercomputer can accommodate. Using the group's newly developed algorithms, Qbox can



Advanced sampling algorithms developed for use with the Qbox quantum simulation code look for rare reactions of interest to researchers. A simulation depicts germanium transitioning suddenly from an ordered crystalline solid to a disordered liquid in response to heat. Green represents germanium atoms. Red and blue represent a high probability and zero probability of electrons, respectively.

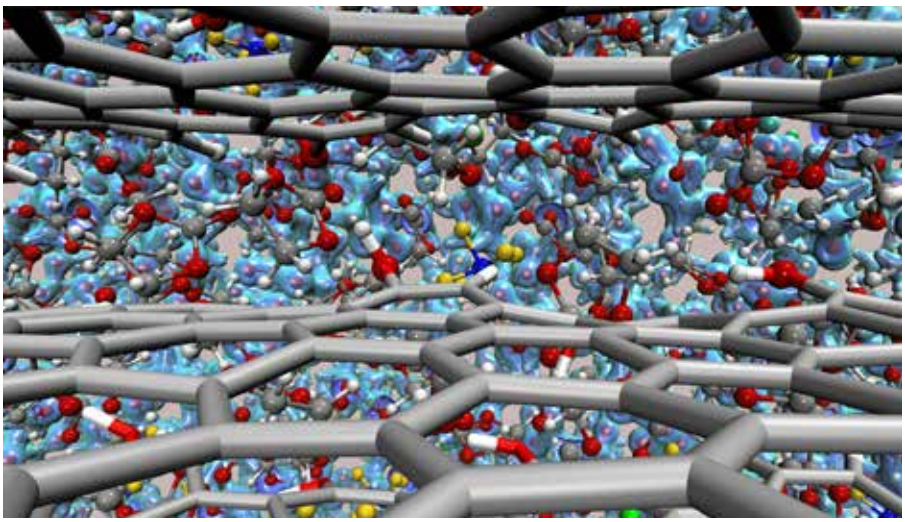
overcome the time limitations of even the most powerful supercomputers with a methodology that is far more computationally efficient than a typical "brute force" approach. Schwegler sees the advanced algorithms accelerating the process of discovery and optimization of new materials properties in the immediate term and, in the longer term, producing data that will be passed to specialized codes designed to work on longer time and length scales. One benefit of this approach would be the ability to predict how materials are likely to perform over decades of use.

Two Computational Breakthroughs

The popular lithium-ion battery is found in products ranging from electric cars to laptop computers. In this battery, the negative electrode is made of graphite, the positive electrode of a metal oxide, and the electrolyte a lithium salt dissolved in an organic solvent. The functioning of the battery depends on the movement of lithium ions between the electrodes. "We aim to achieve a breakthrough in understanding these electrochemical systems," declares Livermore physicist John Pask, who leads an effort including Livermore's Vincenzo Lordi, Erik Draeger, and postdoc Mitchell Ong, along with collaborators from Lawrence Berkeley National Laboratory and UC Berkeley. Divided into two parts, the effort is funded by both BES and the Advanced Scientific Computing Research Program, through the Scientific Discovery through Advanced Computing Program, known as SciDAC.

In the first part, the researchers are developing and implementing two computational breakthroughs in electronic structure methods: discontinuous Galerkin (DG) and pole expansion and selected inversion (PEXSI). Working together, DG and PEXSI overcome the traditional computational bottlenecks faced when researchers attempt to simulate large numbers of atoms using quantum-mechanical methods. The DG technique collapses the size of the matrix problem that must be solved by including both atomic and local-environmental physics into the computation. The PEXSI methodology directly computes electronic density, total energy, and ionic forces without computing individual electronic orbitals, eliminating the usual cubic scaling of solution time with the number of atoms, which has severely limited the physical systems to which quantum mechanics can be applied.

In developing the DG–PEXSI approach, the team first focused on advancing Qbox—increasing its speed and the number of atoms it can simulate—and using the enhanced Qbox code to verify DG–PEXSI at every stage. The team is close to achieving the scales of length (10,000 atoms) and time (50 picoseconds) needed to obtain a detailed quantum-mechanical understanding of the solid–electrolyte interphase layer in lithium-ion batteries, the second main thrust of the project. Progress in improving these batteries has been hindered by an incomplete understanding of the formation and evolution of this critical layer between anode and electrolyte. "No one understands what's going on at the interfaces," says Pask. He explains that although most research is based on experiments, the chemistry is extremely complicated. "To really understand what's going on in the solid–electrolyte interface and other complex, mixed-phase systems, we need quantum-mechanical methods," states Pask. By making quantum-mechanical calculations possible at the necessary length and timescales, DG–PEXSI promises to pave the way for breakthroughs in battery performance, lifetime, and safety. The team's calculations have already shown that the more tightly ions are solvated in an electrolyte, the lower their mobility, contrary to what may be expected based on chemical theory. This discovery alone has the potential to advance the design of lithium-ion battery electrolytes. When complete, DG–PEXSI will be available as open source so that researchers around the world will be able to solve



Livermore's new methodology combining the discontinuous Galerkin (DG) and pole expansion selected inversion (PEXSI) electronic structure methods depicts the interface of a graphite anode (hexagonal mesh) and an electrolyte in a lithium-ion battery. The distance between graphite layers is about 2 nanometers. The DG–PEXSI code promises to obtain a detailed quantum-mechanical understanding of the critical reactions that occur at the anode.

large quantum-mechanical problems currently inaccessible and with less required computation.

Advanced QMC

In the world of simulation, getting as close to reality as possible involves an approach called QMC, which computes the electronic structure of atoms, molecules, and solids to accurately solve Schrödinger's differential equations. Although broadly used to understand the thermodynamic properties of materials, the approach is very expensive in terms of computational horsepower. Miguel Morales-Silva is part of a broad BES-funded effort to develop a next-generation implementation of QMC, called QMCPACK (for "QMC package"), based on continuum real-space QMC. The group is building a platform for theoretical development, broad scientific application, and use in changing computing environments. "QMC used to be a method only for experts," says Morales-Silva. "We want it to become a routine tool for general calculations." The effort includes scientists from Oak Ridge and Argonne national laboratories; Sandia National Laboratories in Albuquerque; and the University of Illinois Urbana-Champaign. At Livermore, Randy Hood, postdoc Roman Nazarov, and graduate student Raymond Clay are also contributing.

QMC methods are first being applied to catalysis, defects, and materials under high pressures, reflecting the research interests of the collaborating institutions. For Livermore, that means determining the equations of state (the relationship between pressure, density, and temperature) of light elements such as hydrogen and hydrogen–helium mixtures, but researchers are working to extend the code's applicability to very heavy elements. Another goal of the project is ensuring that the advanced code keeps up with changing architectures in high-performance computing. For example, newly emerging supercomputers are based on specialized graphics processors instead of central processing units.

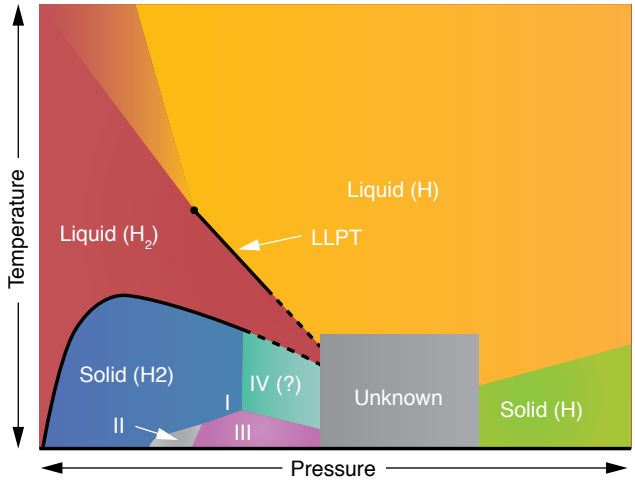
The group is also working to make the code available to a much larger and nonexpert population of investigators. They have made several public releases of the open-source QMCPACK code and developed a QMCPACK website (www.qmcpack.org). The new releases include automation tools that significantly enhance productivity for new and expert users. In 2014, the group organized a training workshop for postdocs and graduate students at Argonne. Another workshop is planned for 2016 at the University of Illinois Urbana-Champaign. In addition, smaller workshops are held regularly for experts in the field.

The outcome of this collaboration is sure to increase productivity and fundamentally alter how QMC data are produced and used by the materials and chemistry community at large. "Our work will provide direct answers to fundamental materials science questions and establish benchmark levels of accuracy," says Morales-Silva.

The Immense Challenges Ahead

The six BES-funded projects at Livermore are an attempt to tackle immense scientific challenges associated with accelerating the fundamental understanding, design, and deployment of new materials and manufacturing processes. The goals are ambitious. For example, advances in simulation and modeling aim to one day enable "chemistry by design" across multiple time and length scales. Livermore researchers are acutely aware that materials and biomaterials research are the foundation for advancing national security and quality of life.

—Arnie Heller



Quantum Monte Carlo calculations are helping to better define the phase diagram of hydrogen (H). Livermore researchers are focusing on the liquid–liquid phase transition (LLPT) from a molecular liquid (H_2, an insulator) to atomic liquid (metal), as well as hydrogen's various crystalline phases, in particular the unknown region near the lower middle part of the diagram.

Key Words: bacteriorhodopsin, carbon nanotube, discontinuous Galerkin (DG), dynamic transmission electron microscope (DTEM), fluctuation electron microscopy (FEM), high-energy x-ray diffraction microscopy, Laboratory Directed Research and Development (LDRD) Program, lithium-ion battery, nanotube porin, Office of Basic Energy Sciences (BES), pole expansion selected inversion (PEXSI), Qbox, QMCPACK, quantum Monte Carlo (QMC), scanning electron microscopy, scanning transmission x-ray microscopy, small-angle x-ray scattering, transmission electron microscopy (TEM).

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